Indian J. Phys. **78(8)**, 729-731 (2004)

AN INTERNATIONAL JOURNAL
IJP

Enhancement in resistivity with annealing temperature in the nanoparticles of Li-Mg ferrite thin films

Sanjukta Ghosh
Department of Physics, University of Calcutta, 92, A P C Road, Kolkata-700 009, India

E-mail: sanjukta999@rediffmail.com

Abstract : Nanocrystalline thin films of $Li_{0.25}Mg_{0.5}Mn_{0.1}Fe_{2.15}O_4$ have been prepared by R F magnetron sputtering technique using Si (100) as substrate. These thin films have been annealed under oxygen atmosphere at 650°C, 700°C, 800°C and 900°C. X-ray diffraction measurement reveals variation in grain sizes proportional to the annealing temperatures. Resistivities of the films have been measured by two-probe method. Interestingly it is observed that resistivity of this ferrite system increases with increase in grain size. Variation in resistivity is explained from the viewpoint of the combining effect of crystal growth and electron-phonon interaction in small volumes.

Keywords : Ferrite thin films, resistivity, crystal growth, electron-phonon interaction.

PACS Nos. : 25.75.-q, 61.82.Ms, 29.17.+w

1. Introduction

Nanocrystalline ferrite thin films are of great interest nowadays due to their versatile applications in the field of magnetic recording media and microwave devices. Nanocrystals present in the films show different magnetic and electric properties than that of bulk due to their exciting fundamental characteristics like small volume, high surface to volume ratio *etc.* Some research works [1-4] on Li and Cu ferrite films have shown lower saturation magnetization and higher coercive fields with respect to the bulk. Properties of thin films may be controlled during deposition by varying the external factors like power, gas-pressure and deposition time. In the present case post-deposition annealing temperature has been varied to get a control over these ferrite films.

2. Experimental outline

2.1 *Sample and thin film preparation :*

The ferrite samples are prepared by standard ceramic technique. The ingredients required are calculated from the chemical formula $Li_{0.25}Mg_{0.5}Mn_{0.1}Fe_{2.15-x}In_xO_4$ (x = 0, 0.3, 0.6, 0.9). Analar grade (AR) Li_2CO_3, $MnCO_3$, $MgCO_3$, In_2O_3 and Fe_2O_3 are used. The stoichiometric ratios of the chemicals are thoroughly mixed in a polypropylene jar containing zirconia balls. Distilled water is taken as the wetting medium. The mixed paste of the chemicals are then carefully taken out and dried in an oven at 300°C. The pre-sintering of the mixed powder is carried out at 750°C in a box furnace and the soaking time is 4 hrs for all the samples. The pre-sintered powder is again subjected to milling for another three hours in the same manner in order to obtain homogeneity in the material. A small quantity of 2% solution of polyvinyl alcohol (PVA) is added to the mixed powder as binding agent. The binder mixed material is dried and then granulated by passing it through sieve of BSS-52 mesh size. The sieved material is pressed under hydraulic pressing technique at the pressure of 1 ton/cm^2 and finally sintered at 1050°C for 12 hours.

Nanocrystalline thin films of $Li_{0.25}Mg_{0.5}Mn_{0.1}Fe_{2.15}O_4$ are deposited on Si (100) substrate using high pressure RF magnetron sputtering technique. The sputtering is carried out in a custom built chamber using a 200 mm long, axial, planar magnetron source. The sputtering target

is a sintered disc (50 mm diameter) prepared by standard ceramic technique placed about 5 cm away from the substrate. The base pressure is better than 1×10^{-6} Torr, while sputtering was carried out in the presence of a mixture of flowing argon and oxygen. Post-deposition annealing is done in oxygen atmosphere at 650°C, 700°C, 800°C and 900°C for 3 hours.

2.2. X-Ray diffraction and resistivity measurement :

XRD pattern for all the films have been collected in the region 20°–65° in steps of 0.1°/min on a Philips diffractometer by Cu (K∝) radiation. Considering the major reflections phase matching is done. The crystallite size calculation has been done following Scherrer equation [5] from full width at half maximum (fwhm) of the strongest reflection *i.e.* (311) peak. An electrometer has been used to carry out resistivity of the films by two-probe method.

3. Results and discussion

Figure 1 clearly indicates at 650°C all the ferrites peaks are not present at proper phase. At 900°C proper crystal structure is noticed. This is an indication of the fact that with increase in annealing temperature crystal growth takes place properly. Height of the strongest reflection (311) peak increases with annealing temperature. Figure 2 shows dependence of crystal size with annealing

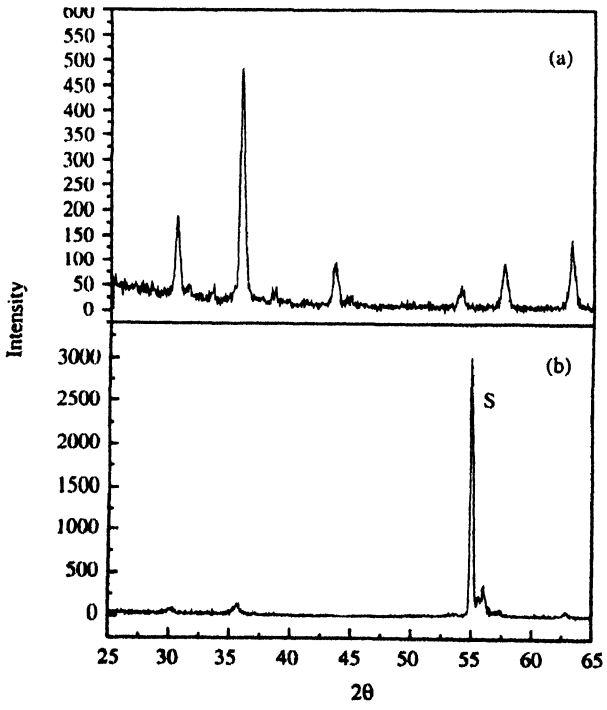

Figure 1. XRD spectra for films annealed at (a) 900°C and (b) 650°C.

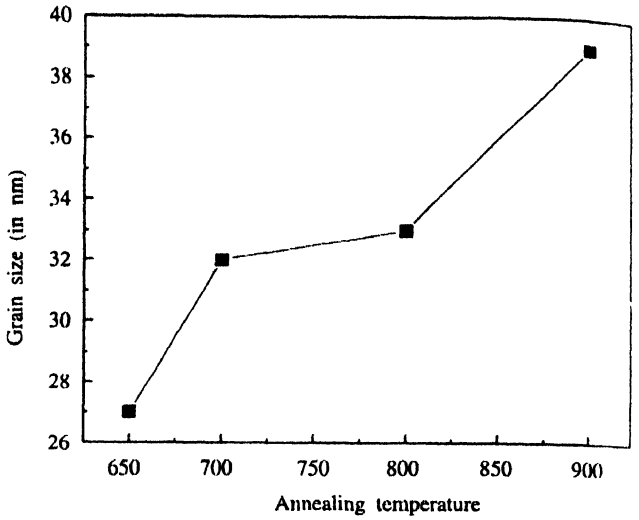

Figure 2. Increase in grain size with annealing temperature.

temperature. Annealing temperature is an important parameter in crystal growth process.

When the films are just produced, they are full of defects like dislocations [6]. The concept of grain boundaries at this stage is quite different and acts as the defect of dislocations. At this initial stage when the crystals are just produced, they remain in dynamic equilibrium with their parent phase, which leads to minimum free energy. No growth occurs at this stage. This equilibrium get disturbed for growth to occur if there is any change in temperature, pressure, chemical potential or strain.

Any one of these parameters acts as driving force if it is held minimally away from its equilibrium value. At the present case, it is the post-deposition annealing temperature. The system then releases energy to the surroundings to compensate for the decrease in entropy occasioned by ordering of atoms in the crystal and evolution of heat of crystallization. Basically, crystallization is a two-step non-equilibrium process (a) primary crystallization and (b) secondary crystallization. At the initial stage of crystallization, nucleation process is not favourable as very less number of crystals exists and this increases the surface to volume ratio of the system. Therefore, the dangling bonds present in the system are responsible to collect energy from surroundings to the surface. This gives rise to nucleation of a new phase though this is a discontinuous process. When the crystals are new born, they grow rapidly and introduce defects. This is observed in Figure 1(b) where the structure is not fully crystalline. These defects more or less get annihilated

due to annealing temperature. In the second step of grain growth, the interesting phenomenon involved is migration of high-angle grain boundaries. High-angle grain boundaries are the defects created due to dislocations. Some energy is stored in the form of high-angle grain boundaries during primary crystallization. At this stage, reduction in the stored energy act as the driving force for decrease in percentage of high angle grain boundaries. Due to mobile nature of high-angle grain boundaries, they either collapse or take a smaller curvature supported by thermal activation [7]. This reduces the volume fraction of high-angle grain boundaries causing an overall decrease in the grain boundary volume. This increases the crystal size as noticed here at 900°C. Consequently, a decrease in overall inhomogeneity in the films takes place with XRD peak reflections in proper phase. Therefore with increase in grain or crystal size, low-angle grain boundaries migrate over high angle grain boundaries. Small angle grain boundaries do not collapse at even high annealing temperature, as they are less mobile with respect to high-angle grain boundaries according to grain growth kinetics. This process explains how grain size increases with annealing temperature. Grain sizes can reach an optimum value for a particular deposition condition.

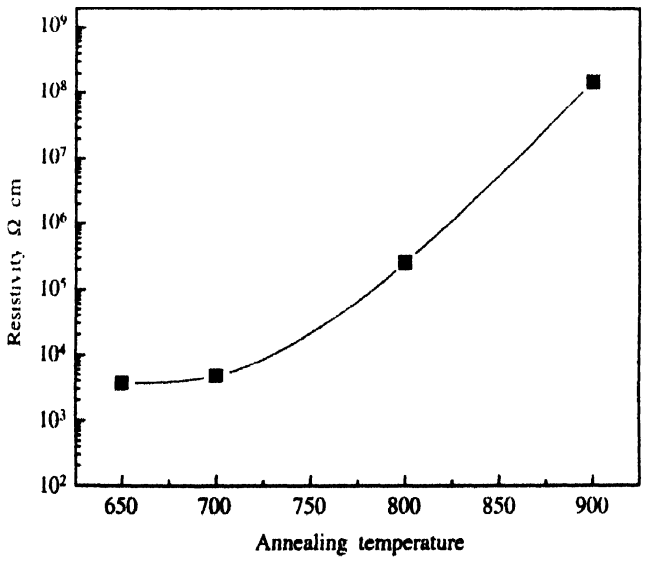

Figure 3. Variation in resistivity with increase in annealing temperature.

Two-probe resistivity measurement shows that resistivity increases with increase in grain size. Another important factor that has to include is the electron-phonon coupling. This phenomenon has also been explained in details in our earlier report [8]. Diameters of the smaller grains become comparable to the mean characteristic length of phonons [9]. This degrades the probability of electron-phonon scattering inside the grains. The physically significant term resistance arises as a result of electron-phonon interaction. Thus for low-grain sizes resistance of the system becomes quite low. When grain growth takes place with increase in annealing temperature the diameter of the grains become higher than the wavelength of phonons. This enhances the probability of electron phonon scattering inside the grains. Consequently, an increase in value of resistivity is noticed. Therefore in the case of ferrite films, it is clearly explained why with increase in annealing temperature resistivity increases.

4. Conclusion

It is very clear from grain growth kinetics that crystal size increases with annealing temperature due to migration of low-angle grain boundaries over high-angle grain boundaries. Grain growth enhances the electron-phonon coupling and as a consequence resistivity of the system increases.

Acknowledgment

Author is grateful to Late Prof. D Banerjee (CU) and Dr. P Ayyub for supporting in thin film preparation. Author thanks UGC and Nuclear Science Centre for financial support.

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